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Hydrogen-Permselective TiO_2/SiO_2 Membranes Formed by Chemical Vapor Deposition

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Abstract : Films of TiO_2/SiO_2 were deposited on the inner surface of the porous glass support tubes by decomposition of tetraisopropyl titanate (TIPT) and tetraethyl orthosilicate (TEOS) at atmospheric pressure. Dense and hydrogen-permselective membranes were formed at 400-600℃. The permeation rates of H_2 through the membrane at 600℃ were 0.2-0.4 cm^3(STP)/min-cm^2-atm and H_2:N_2 permeation ratios were above 1000. The permeation properties of the membranes were investigated at various deposition temperatures and TIPT/TEOS concentrations. Decomposition of TIPT alone at temperatures above 400℃ produced porous crystalline TiO_2 films and they were not H_2-selective. Decomposition of TEOS produced H_2-permeable SiO_2 films at 400-600℃ but film deposition rate was very low. Addition of TIPT to the TEOS stream significantly accelerated the deposition rate and produced highly H_2-selective films. Increasing the TIPT/TEOS concentration ratio increased the deposition rate. The TiO_2/SiO_2 membranes formed at 600℃ have the permeation properties comparable to those of SiO_2 membranes produced from TEOS.

Keywords :

1. Introduction

Considerable efforts have been made to develop highly H_2-permselective membranes by applying selective inorganic materials such as Pd or SiO_2 on microporous supports. These membranes can be used at high temperatures in membrane-reactor configurations to improve the conversion of equilibrium-limited dehydrogenation reactions. H_2-permselective SiO_2 membranes, in particular, have been successfully fabricated using chemical vapor deposition technique on a variety of porous supports [1-7]. Thin SiO_2 layer imbedded in the microporous support showed sufficient selectivity for hydrogen but suffered from densification accompanied by reduction in permselectivity when subject to thermal treatment especially in the presence of water [8,9]. For practical application these membranes should have high selectivity, adequate permeation rate and stability. To improve the chemical stability of SiO_2 membranes, binary system of SiO_2 with Al_2O_3, TiO_2 and ZrO_2 has been investigated [10]. It has been known that the addition of TiO_2 to SiO_2 films produces mixed oxides of high resistance and stability for optical application [11]. In TiO_2-SiO_2 binary glass system the free volume is known to be increased

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by substitution of TiO_2 for SiO_2 leading to increase the helium mobility [12].

In this paper we present experimental results on the formation of TiO_2/SiO_2 membranes on the porous glass supports using a chemical vapor deposition technique. Effects of experimental variables on the deposition process and permeation properties of the membranes were investigated.

2. Experimental

Tetraisopropyl titanate (TIPT, $Ti[OCH(CH_3)_2]_4$, 99.99%) and tetraethyl orthosilicate (TEOS, $Si[OC_2H_5]_4$, 99.99%) were used as received from Aldrich Co. Vycor glass tubes obtained from Corning Glass Inc. have 7-mm outside diameter, 1.1-mm wall thickness, 0.28 void fraction and 40Å mean pore diameter.

The apparatus and procedure for film deposition are similar to those for SiO_2 film deposition from TEOS described elsewhere [5]. TIPT and TEOS carried by N_2 flowing through the bubblers were introduced into the inner region of the porous glass tube with separate O_2/N_2 stream. Concentrations of TIPT and TEOS were controlled either by regulating the flow rate of corresponding carrier gas or by regulating the temperature of the bubbler. The total flow rate was 900cc/min. Typical concentrations of TEOS and O_2 in N_2 stream were 0.05% and 22.22% respectively. The concentration of TIPT was adjusted so that TIPT/TEOS concentration ratio varied between 0.1 and 7. Deposition was carried out at temperature range between 400 and 600℃. The pressure at both sides of the porous Vycor tube was 1 atm.

The permeation rates of H_2 and N_2 through the membrane after each deposition interval were measured by a bubble flow meter or a pressure transducer [5]. Permeation rate (Q) was defined as the flux of a gas through the outer surface area of the support tube when pressure difference was 1 atm. The morphology and composition of the films were analyzed by scanning electron microscopy (SEM), electron microprobe analysis (EPMA), and x-ray photoelectorn spectroscopy (XPS).

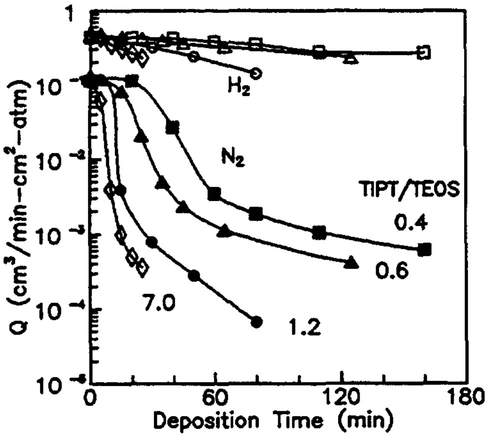


Fig. 1. Evolution of H_2 and N_2 permeation rates during the deposition at 600℃ and at various TIPT/TEOS concentrations (O_2: 22.22% in N_2).

3. Results and Discussion

3.1. Effect of TIPT/TEOS concentrations

TiO_2/SiO_2 membranes were formed on the inner surface of the porous Vycor tubes by introducing TEOS and TIPT vapor simultaneously into the reactor with O_2/N_2 stream. Figure 1 shows the evolution of H_2 and N_2 permeation rates during the deposition at 600℃ and at various TIPT/TEOS concentrations. During the film deposition, permeation rate of N_2 decreased rapidly while that of H_2 decreased gradually. H_2:N_2 permeation ratio increased from 3.7 to more than 100 showing that dense H_2-selective layer was formed. The rapid decrease in the permeation rate of N_2 indicates that almost all of the pores of the support are plugged up. Pore plugging may be defined as the point where the permeation rate of N_2 is 1% of its initial value. Table 1 summarizes the time to pore plugging as a function of TIPT/TEOS concentrations. The time to pore plugging decreases with increasing TIPT concentration indicating that increase in TIPT concen

Table 1. Time to pore plugging at various TIPT/TEOS concentrations during the deposition at 600℃ (O_2 concentration : 22.22% in N_2).

Concentration (%)		Time to pore plugging
TIPT	TEOS	
0	0.05	more than 10 hr
0.02	0.05	113 min
0.03	0.05	68 min
0.06	0.05	26 min
0.36	0.05	14 min
0.36	0	no pore plugging occurred

tration increases the deposition rate of TiO_2/SiO_2 layer. Permeation rate of H_2 at the time of pore plugging, however, decreases with increasing TIPT concentration. XPS analysis of the film reveals that the amount of Ti in the film increases with increasing TIPT concentration in the reactant.

One thing to be noteworthy is the deposition rate of the TiO_2/SiO_2 layer compared to that of the pure SiO_2 layer. The deposition rate of SiO_2 by TEOS decomposition in the absence of TIPT was much lower than the rate of TiO_2/SiO_2 deposition. Addition of TIPT to the TEOS stream significantly accelerated the deposition rate suggesting that decomposition of TEOS can be catalyzed by TIPT present in the reactor environment. Aitchison et al. reported the catalytic effect of TIPT on the decomposition of TEOS in TiO_2/SiO_2 film growth at low pressure [13]. They asserted that the reaction leading to the formation of TiO_2/SiO_2 films are dominated by reactive surface intermediate which may consist of partially decomposed organic or metalorganic species or of particularly reactive surface sites generated during the film growth. The experiment in this study has been carried out at atmospheric pressure and there may be intermediates formed in the gas phase by the reaction of TIPT and TEOS before their deposition at the surface.

The other interesting aspect of the result is that decomposition of TIPT alone cannot produce H_2-selective layers whereas addition of TEOS

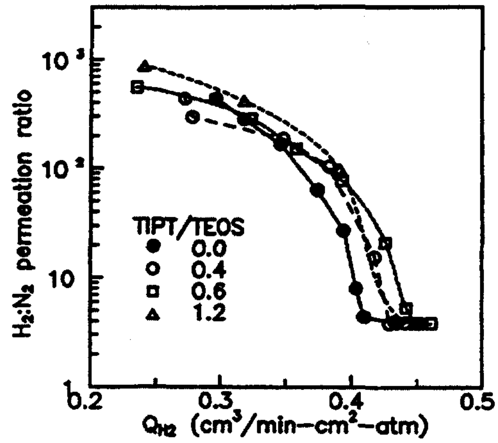


Fig. 2. H_2:N_2 permeation ratio against H_2 permeation rate (Q_{H2}) during the deposition at 600℃.

produced highly H_2-permeable films. Decomposition of TIPT alone at temperatures above 400℃ produced porous crystalline TiO_2 films and they were not H_2-selective [14]. Crystallization of TiO_2 may be inhibited by TEOS molecules or intermediates of TEOS present in the reactor environment during the deposition reaction, producing amorphous H_2-permeable films of TiO_2/SiO_2.. The true mechanism for the inhibition of crystallization by TEOS are not clear at present. But, considering the fact that formation of crystalline phase is possible when the homogeneous reaction mechanism is dominant, it may be deduced that the inhibition of TiO_2 crystallization by TEOS is accomplished at the stage of homogeneous reaction between TIPT and TEOS to form oligomers in the gas phase.

The performance of the membranes during the deposition can be easily compared by plotting a selectivity (H_2:N_2 permeation ratio in this study) vs. H_2 permeation rate. A desirable membrane is one that has high permeability as well as high selectivity. As shown in Figure 2 there is no significant difference in performance among the membranes produced at different ratios of TIPT/TEOS. The TiO_2/SiO_2 membranes formed at 600℃ have the permeation properties comparable to those of SiO_2 membrane.

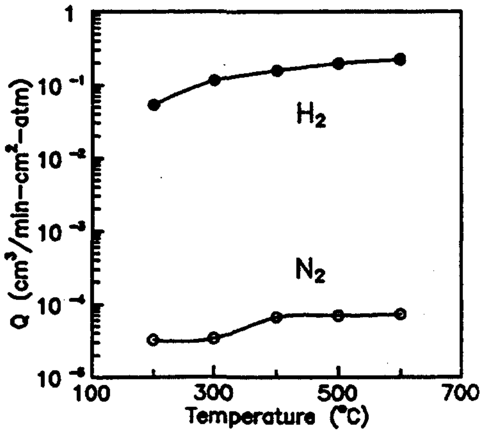


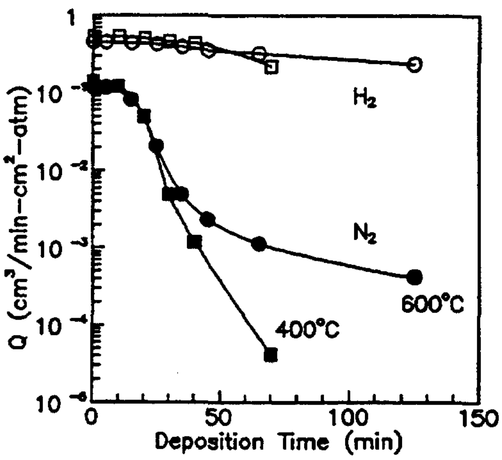
Fig. 3. Effect of temperature on the permeation rate (Q) of H_2 and N_2 through the TiO_2/SiO_2 membrane.

3.2. Effect of temperature on the permeation rate

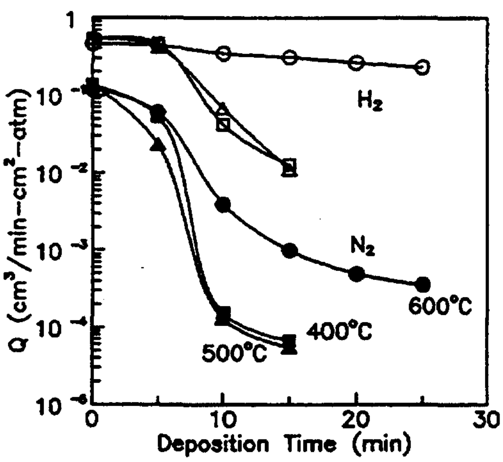
Permeation rates of H_2 and N_2 through a TiO_2/SiO_2 film deposited at 600℃ and TIPT/TEOS ratio of 0.1 were measured at five different temperatures and the result is shown in Figure 3. Before the measurement the membrane has been subjected to thermal treatment at 700℃ under dry N_2 for 3 days to get reproducible result on the permeation rate. The permeation rates of both gases increases with increasing temperature indicating that permeations of H_2 and N_2 is governed by activated diffusion process. The calculated activation energy for H_2 permeation through the membrane is 8 kJ/mol which is close to the value for SiO_2 films produced from TEOS (6 kJ/mol) [5].

3.3. Effect of the deposition temperature

Deposition experiments were carried out at 400-600℃ using two different concentration ratios of TIPT/TEOS. Figure 4 shows the progress of pore plugging during the deposition reaction. When TIPT/TEOS concentration ratio was 0.6, the time to pore plugging at 400℃ and 600℃ were 40 min and 70 min, respectively. When TIPT/TEOS ratio increased to 7.0, the time to pore plugging decreased to about 8 min at 400-500℃, and it became 15 min at 600℃. The lower deposition rate found in both experiments at 600℃ may be ascribed to the homogeneous reaction of TIPT in the gas phase. As mentioned in the previous section the film deposition rate was closely related to the TIPT concentration in the reactant. It was found from the previous experiment that decomposition of TIPT at



(a)

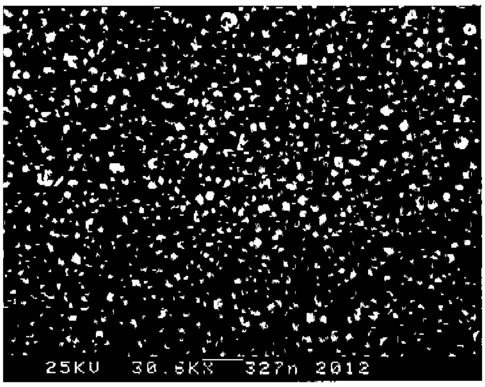


(b)

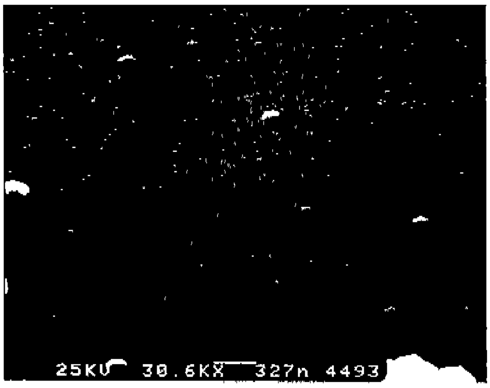
Fig. 4. Evolution of H_2 and N_2 permeation rate (Q) during the deposition at various temperatures. TIPT/TEOS concentration ratio was (a) 0.6 and (b) 7.0. TEOS and O_2 concentration were 0.05% and 22.22% in N_2, respectively.

temperatures above 400℃ produced not only porous crystalline TiO_2 films but also TiO_2 particles via homogeneous reaction [14]. Therefore, as deposition temperature increases, more amount of TIPT could be consumed by homogeneous reaction for particle formation and only a small fraction of TIPT could participate in the film formation, resulting in a lower pore plugging rate. XPS analysis of the film produced under TIPT/TEOS concentration ratio of 7.0 showed that the film deposited at 400℃ had 18.1% Ti while the film deposited at 600℃ had 10.4% Ti, confirming the depletion of TIPT available for deposition at 600℃.

In the case of SiO_2 membranes formed by CVD of TEOS [5], the higher deposition temperature produced the denser film with the higher H_2/N_2 selectivity. For TiO_2/SiO_2 membranes, however, H_2/N_2 selectivity of the membrane seems to be a complicated function of deposition temperature and concentration ratio of TIPT/TEOS. For example, when TIPT/TEOS ratio was 0.6, the film produced at 400℃ had higher selectivity than the film deposited at 600℃ as shown in Figure 4-a. On the other hand, when TIPT/TEOS ratio increased to 7, H_2/N_2 selectivity increased as the deposition temperature increased from 400℃ to 600℃ as shown in Figure 4-b. Permeation characteristics of TiO_2/SiO_2 membranes depend on the amount of TiO_2 in the membrane. Under the experimental condition employed in this study, deposition at 600℃ produced the membranes with Ti content less than 11% and the H_2/N_2 selectivity of the membranes were similar as shown in Figure 2. Under the same experimental condition, deposition at 400℃ produced membranes having Ti content up to 18% and H_2/N_2 selectivity of the membranes varied with TIPT/TEOS ratio. Besides the amount of TiO_2, TiO_2 structure in the membrane may affect the permeation characteristics. In case TiO_2 exists in a crystalline structure, it would have negative effect on the selectivity of the TiO_2/SiO_2 membrane. Further work is required to elucidate the effect of the content and structure of TiO_2 on the permeation characteristics of the TiO_2/SiO_2 membranes.



(a)



(b)

Fig. 5. SEM micrographs of the inner surface of porous glass tubes. (a) after TiO_2 film deposition and (b) after TiO_2/SiO_2 film deposition at 400℃

3.4. Characterization or the films by SEM and EPMA

Microstructure of the films were characterized by SEM. Figure 5-a is a surface morphology of pure TiO_2 films produced at 400℃ showing a typical crystalline structure of TiO_2 film. As mentioned before, the films are porous and did not show any selectivity to H_2. In contrast, the TiO_2/SiO_2 films shown in Figure 5-b manifests a smooth surface which is much different from crystalline TiO_2 films. The surface morphology of TiO_2/SiO_2 films are almost the same regardless of the TIPT/TEOS ratio and deposition temperature employed in the experiments. Ti mapping of the surface of TiO_2/SiO_2 film by

EPMA shows that Ti is uniformly distributed on the surface.

4. Conclusion

Films of TiO_2/SiO_2 were deposited on the inner surface of the porous glass tubes by the decom position of tetraisopropyl titanate (TIPT) and tetraethyl orthosilicate (TEOS) at atmospheric pressure. Dense and hydrogen-permselective membranes were formed at 400-600℃. Addition of TIPT to the TEOS stream significantly accelerated the deposition rate and produced highly H_2-selective films. Increasing the TIPT/TEOS ratios increased the deposition rate. At temperatures above 400℃ decomposition of TIPT produced porous crystalline TiO_2 films. In the presence of TEOS, however, crystallization of TiO_2 appeared to be inhibited and highly H_2-permeable films were formed. The TiO_2/SiO_2 membranes formed at 600℃ have the permeation properties comparable to those of SiO_2 membranes formed from TEOS.

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